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(54) Stabilised polymer compositions

(57) There are disclosed novel halogenated polymer compositions comprising

- (a) 100 parts of a chlorinated thermoplastic,
- (b) 0.7 to 2 parts of thiodiethylene glycol bis (acetoacetate) of formula  $(H_3CCOCH_2COOCH_2CH_2)_2S$ ,
- (c) 0 to 0.5 part of at least one calcium, barium and/or magnesium salt of an aliphatic  $C_6-C_{24}$  monocarboxylic or  $C_6-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- (d) 0.01 to 0.2 part of at least one zinc salt of an aliphatic  $C_6-C_{24}$  monocarboxylic or  $C_6-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- (e) 3 to 10 parts of epoxidised unsaturated fatty acid esters, and
- (f) 10 to 70 parts of at least one organic plasticiser.

These compositions can be used, in particular, for the preparation of PVC sheets for food packaging.

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Stabilised polymer compositions

The present invention relates to stabilised compositions of chlorinated thermoplastics which contain an organic plasticiser as well as thiodiethylene glycol bis(acetoacetate), epoxidised unsaturated fatty acid esters, a zinc carboxylate and, optionally, a calcium, barium and/or magnesium carboxylate as stabiliser.

Mixtures of stabilisers of  $\beta$ -keto esters of diols and polyols having thioether structure and metallised stabilisers, for example calcium and zinc carboxylates, are disclosed in US patent 4 327 000. These mixtures are, in principle, effective stabilisers for chlorinated thermoplastics, for example PVC and PVC-containing polymers. In this US patent specification, thiodiethylene glycol bis(acetoacetate) is cited as an example of the  $\beta$ -keto esters. Despite their intrinsically interesting properties, it has so far not been possible to commercialise the stabilisers disclosed in US patent 4 327 000, as their action has proved insufficient for practical purposes. In particular, the polymers stabilised therewith underwent somewhat too pronounced yellowing, especially when subjected to prolonged exposure to heat. In addition, the transparency of the articles fabricated with the aid of the stabilised polymers was not entirely satisfactory. These observations also apply to the two stabiliser mixtures specifically described in Application Examples A and B of US patent 4 327 000, especially also as regards initial colour and colour retention. Similar compositions are also disclosed in Japanese Patent Kokai Sho-54 11948, but they additionally contain free aromatic carboxylic acids. None of the two cited publications discloses stabilised PVC compositions that contain a plasticiser. They therefore teach only the stabilisation of rigid PVC, the morphology of which, however, differs radically from that of plasticised PVC.

It has now been found that the properties of stabiliser mixtures which contain components disclosed in US patent 4 327 000 can be enhanced in such a manner that they are suitable for industrial use and that they are particularly suitable for stabilising plasticised, chlorinated thermoplastics. Surprisingly, this enhancement can be achieved by combining a quite specific  $\beta$ -keto ester with zinc and, optionally, calcium, barium and/or magnesium carboxylate primary stabilisers in very specific concentrations and ratios.

Accordingly, the present invention relates to stabilised polymer compositions comprising

- a) 100 parts of a chlorinated thermoplastic,
- b) 0.7 to 2 parts of thiodiethylene glycol bis(acetoacetate) of formula  $(H_3CCOCH_2COOCH_2CH_2)_2S$ ,
- c) 0 to 0.5 part of at least one calcium, barium and/or magnesium salt of an aliphatic  $C_8-C_{24}$  monocarboxylic or  $C_8-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- d) 0.01 to 0.2 part of at least one zinc salt of an aliphatic  $C_8-C_{24}$  monocarboxylic or  $C_8-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- e) 3 to 10 parts of epoxidised unsaturated fatty acid esters, and
- f) 10 to 70 parts of at least one organic plasticiser.

The amount of thiodiethylene glycol bis(acetoacetate) [component b)] contained in the polymer composition is preferably 0.7 to 1.5 parts, more particularly 0.8 to 1.3 parts and, most preferably, about 1 part.

Component c) is preferably present in a concentration of 0 to 0.4 part, for example 0 to 0.35 part. The compositions of this invention preferably contain a component c) (concentration  $> 0$ ). In this case, component c) is present in an amount of 0.001 to 0.5 part, preferably 0.01 to 0.5 part, more particularly 0.05 to 0.4 part and, most preferably, 0.1 to 0.35 part. Very good results are also obtained with amounts of 0.05 to 0.15 part.

Component c) is a calcium, barium or magnesium salt or a mixture of said salts, preferably a calcium or magnesium salt and, most preferably, a calcium salt, of an aliphatic monocarboxylic or hydroxymonocarboxylic acid of 8 to 24 carbon atoms or of benzoic acid or tert-butylbenzoic acid.

The aliphatic monocarboxylic or hydroxymonocarboxylic acids are saturated or unsaturated and contain preferably 8 to 22 carbon atoms. The preferred hydroxycarboxylic acid is hydroxystearic acid, for example 12-hydroxystearic acid. Preferred monocarboxylic acids are 2-ethylhexanoic acid, neodecanoic acid, lauric acid, stearic acid and behenic acid. Component c) is preferably calcium, barium and/or magnesium octoate, preferably calcium and/or magnesium octoate and, most preferably, calcium octoate (salt of 2-ethylhexanoic acid), calcium laurate, calcium stearate or calcium behenate. It will be readily understood that mixtures of salts of different acids can also be used.

The amount of component d) in the polymer compositions is preferably 0.05 to 0.2 part, most preferably 0.1 to 0.2 part. Component d) is the zinc salt of an aliphatic monocarboxylic or hydroxymonocarboxylic acid of 8 to 24 carbon atoms or of benzoic acid or tert-butylbenzoic acid. The aliphatic monocarboxylic or hydroxymonocarboxylic acids are saturated or unsaturated and contain preferably 8 to 22 carbon atoms. The preferred hydroxycarboxylic acid is hydroxystearic acid, for example 12-hydroxystearic acid. Preferred monocarboxylic acids are 2-ethylhexanoic acid, lauric acid, stearic acid and behenic acid. Component d) is preferably zinc octoate (salt of 2-ethylhexanoic acid), basic zinc octoate, zinc stearate, zinc neodecanoate, zinc laurate, zinc behenate or zinc benzoate, and is most preferably zinc octoate, basic zinc octoate, zinc neodecanoate, zinc stearate or zinc benzoate. Zinc stearate will most preferably be used in an amount of about 0.2 part, zinc octoate in an amount of about 0.1 part, and basic zinc octoate in an amount of about 0.05 part.

The polymer compositions contain component e) preferably in an amount of 4 to 7 parts, most preferably of about 5 parts. Component d) is preferably epoxidised soybean oil.

The compositions of the invention preferably contain component f) in an amount of 15 to 70 parts, for example 15 to 60 parts and, most preferably, 20 to 50 parts. Epoxidised fatty acid esters (component e)) are also often called plasticisers. It must be emphasised that the definition of component f) (plasticiser) does not comprise these esters. Components e) and f) are therefore different.

Examples of suitable organic plasticisers are those selected from the following groups:

A) Phthalates (phthalic acid esters)

Examples of such plasticisers are: dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, di-2-ethylhexylphthalate, di-n-octyl phthalate, diisooctyl phthalate, diisononyl phthalate, diisodecyl phthalate, diisotridecyl phthalate, dicyclohexyl phthalate, dimethylcyclohexyl phthalate, dimethyl glycol phthalate, dibutyl glycol phthalate, benzylbutyl phthalate and diphenyl phthalate, as well as mixtures of phthalates such as C<sub>7</sub>-C<sub>9</sub>alkyl phthalates and C<sub>9</sub>-C<sub>11</sub>alkyl phthalates from mainly linear alcohols, C<sub>6</sub>-C<sub>10n</sub>-alkyl phthalates and C<sub>8</sub>-C<sub>10n</sub>-alkyl phthalates. Preferred phthalates are dibutyl phthalate, dihexyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, diisooctyl phthalate, diisononyl phthalate, diisodecyl phthalate, diisotridecyl phthalate and benzylbutyl phthalate, as well as the cited mixtures of alkylphthalates. Di-2-ethylhexyl phthalate (DOP) is especially preferred.

B) Esters of aliphatic dicarboxylic acids, in particular esters of adipic, azelaic and sebacic acid

Examples of such plasticisers are: di-2-ethylhexyl adipate, diisooctyl adipate (mixture), diisononyl adipate (mixture), diisodecyl adipate (mixture), benzylbutyl adipate, benzyloctyl adipate, di-2-ethylhexyl azelate, di-2-ethylhexyl sebacate and diisodecyl sebacate (mixture). Di-2-ethylhexyl adipate and diisooctyl adipate are preferred.

### C) Trimellitates

Examples are: tri-2-ethylhexyl trimellitate, triisodecyl trimellitate (mixture), triisotridecyl trimellitate, triisooctyl trimellitate (mixture), as well as tri-C<sub>1</sub>-C<sub>6</sub>alkyltrimellitate, tri-C<sub>6</sub>-C<sub>10</sub>alkyltrimellitate, tri-C<sub>7</sub>-C<sub>9</sub>alkyltrimellitate and tri-C<sub>9</sub>-C<sub>11</sub>alkyltrimellitate. The last mentioned trimellitates are formed by esterification of trimellitic acid with the appropriate alkanol mixtures. Preferred trimellitates are tri-2-ethylhexyl trimellitate and the cited trimellitates from mixtures of alkanols.

### D) Polyesters (polymer plasticisers)

A definition of these plasticisers and examples thereof will be found in "Plastics Additives Handbook", edited by H. Gächter and H. Müller, Hanser Publishers, 1985, page 284, Chapter 5.7.10, and in "PVC Technology", edited by W.V. Titow, 4th Ed., Elsevier Publishing Co., 1984, pp. 165 - 170. The commonest starting materials for the preparation of the plasticisers are: dicarboxylic acids such as adipic acid, phthalic acid, azelaic acid, and sebacic acid; diols such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and diethylene glycol; monocarboxylic acids such as acetic acid, capric acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, pelargonic acid and benzoic acid; monofunctional alcohols such as isooctanol, 2-ethylhexanol, isodecanol and mixtures of C<sub>7</sub>-C<sub>9</sub>alkanols and mixtures of C<sub>9</sub>-C<sub>11</sub>alkanols. Particularly useful polyester plasticisers are those obtained from the cited dicarboxylic acids and monofunctional alcohols.

### E) Phosphates

A definition of these esters will be found in the "Plastics Additives Handbook" referred to above on page 271, Chapter 5.7.2. Examples of such phosphates are: tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylhexyl phosphate, trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate. The preferred phosphate is tri-2-ethylhexyl phosphate.

F) Chlorinated hydrocarbons (paraffins).

G) Hydrocarbons.

H) Monoesters, for example butyl octoate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulfonates.

I) Glycol esters, for example diglycol benzoates.

Definitions and examples of plasticisers of groups F) to I) will be found in the following handbooks:

"Plastics Additives Handbook", edited by H. Gächter and H. Müller, Hanser Publishers, 1985, page 284, Chapter 5.7.11 (group F), and Chapter 5.7.13 (group G);

"PVC Technology", edited by W.V. Titow, 4th Ed., Elsevier Publishing Co., 1984, pp. 171 - 173, Chapter 6.10.2 (group F), page 174, Chapter 6.0.5 (group G), page 173, Chapter 6.10.3 (group H) and pages 173 - 174, Chapter 6.10.4 (group I).

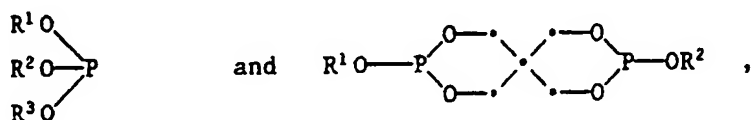
Particularly preferred plasticisers are those of groups A) to E), especially those of groups A) to C) and, first and foremost, the plasticisers of these groups singled out as preferred. Di-2-ethylhexyl phthalate (DOP) is especially preferred.

The chlorinated thermoplastic polymers (component a)) stabilised according to this invention are preferably vinyl chloride homopolymers (PVC), copolymers of vinyl chloride with unsaturated comonomers (PVC copolymers), mixtures of the cited polymers with one another or mixtures of the cited polymers with other homo- or copolymers.

Among the vinyl chloride homo- and copolymers, suspension and mass polymers as well as emulsion polymers are to be singled out for special mention. Examples of suitable comonomers for the copolymers are: vinyl acetate, vinylidene chloride, trans-dichloroethylene, ethylene, propylene, butylene, maleic acid, acrylic acid, fumaric acid, and itaconic acid. Further suitable chlorinated polymers are post-chlorinated PVC and

chlorinated polyolefins, and also graft polymers of PVC with ABS, EVA and MBS. Suitable mixtures are, in particular, those of PVC homo- and copolymers with ABS, NBR, NAR, SAN and EVA.

The compositions of this invention can also contain further stabilisers conventionally added to chlorinated thermoplastics. Thus, for example, they contain 0 to 3 parts, preferably 0 to 1.5 parts and, most preferably, 0 to 1 part, of one or more phosphites. Such phosphites may be present in an amount of ca. 0.01 to 3 parts, preferably 0.01 to 1.5 parts, for example 0.01 to 1 part, preferably 0.1 to 0.6 part, for example 0.2 to 0.5 part. Examples of such phosphites are those of formulae



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are identical or different and are  $\text{C}_6$ - $\text{C}_{18}$ alkyl,  $\text{C}_6$ - $\text{C}_{18}$ alkenyl, a substituted or unsubstituted phenyl radical or  $\text{C}_5$ - $\text{C}_7$ cycloalkyl.

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  as  $\text{C}_6$ - $\text{C}_{18}$ alkyl are, for example, n-hexyl, n-octyl, n-nonyl, decyl, dodecyl, tetradecyl, hexadecyl or octadecyl. Alkyl groups of 8 to 18 carbon atoms are preferred.

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  as substituted phenyl are, for example, tolyl, ethylphenyl, xylyl, cumyl, cymyl, cresyl, 4-methoxyphenyl, 2,4-dimethoxyphenyl, ethoxyphenyl, butoxyphenyl, p-n-octylphenyl, p-n-nonylphenyl or p-n-dodecylphenyl.

Particularly suitable phosphites are trioctyl, tridecyl, tridodecyl, tritetradecyl, tristearyl, trioleyl, triphenyl, tricresyl, tris-p-nonylphenyl or tricyclohexyl phosphite; and particularly preferred phosphites are the aryl dialkyl phosphites and the alkyl diaryl phosphites, for example phenyl didecyl phosphite, 2,4-di-tert-butylphenyl didodecyl phosphite, (2,6-di-tert-butylphenyl)didodecyl phosphite, and the dialkyl pentaerythrityl diphosphites and diaryl pentaerythrityl diphosphites, such as distearyl pentaerythrityl diphosphite.

Preferred organic phosphites are distearyl pentaerythrityl diphosphite, trisnonylphenyl phosphite and phenyl didecyl phosphite.

The compositions of the invention can also contain further known co-stabilisers, for example 0 - 2 parts, in particular 0 - 1.5 parts. They are in this case preferably present in an amount of 0.01-2, more particularly 0.05-1.5, for example 0.1-1, and most preferably 0.1-0.5, parts. Suitable costabilisers of this type are aminocrotonates, dehydracetic acid, 1,3-diketo compounds, 2,4-dihydroxybenzophenone, 2,4-dihydroxy-4'-tert-butylbenzophenone and pyrrole derivatives, which last-mentioned compounds are preferred.

Particularly suitable aminocrotonates are the esters with monohydric, linear C<sub>8</sub>-C<sub>20</sub>alcohols, especially C<sub>12</sub>-C<sub>18</sub>alcohols, and/or with 1,3-butanediol or 1,4-butanediol and/or 1,2-dipropylene glycol and/or thiodiethylene glycol.

1,3-Diketo compounds suitable for use as co-stabilisers are preferably those described in DE-B 2 600 516 and EP-A 35 268, for example those of the formula indicated in the patent claim of DE-B 2 600 516. Preferred 1,3-diketo compounds are benzoylstearyl methane, alkyl (for example ethyl) 2-benzoylacetoacetate and triacylmethanes.

Particularly suitable pyrrole co-stabilisers are those described in EP-A 22 087 and GB-A 2 078 761, for example those of formula I indicated therein, preferably the pyrrole derivatives defined in claims 2 - 9 of EP-A 22 087. 2-Methyl-3-cyclohexyloxycarbonyl-4-phenyl-1H-pyrrole may be cited by way of example.

In addition to the above-mentioned optional co-stabilisers, or in place thereof, the compositions of the invention can contain further optional components, for example organotin stabilisers, for example butyl thiostannonic acid, mono-[n-octyl]tin tris[isooctylthioglycolate], di-n-octyltin bis[isooctylthioglycolate], dibutyltin sulfide, dibutyltin thioglycolate or monobutyltin sulfide and monomethyltin tris[alkylthioglycolate], mono[n-butyl]tin tris[alkylthioglycolate], mono[carb-n-

butoxy-ethyl]tin tris[alkylthioglycolate], bis[methyl]tin bis[alkylthioglycolate], bis[n-butyl]tin bis[alkylthioglycolate], bis[carb-n-butoxyethyl]tin bis[alkylthioglycolate], monomethyltin tris[alkylthiopropionate], mono[n-butyl]tin tris[alkylthiopropionate], mono[carb-n-butoxyethyl]tin tris[alkylthiopropionate], bis[methyl]tin bis[alkylthiopropionate], bis[n-butyl]tin bis[alkylthiopropionate] and bis[carb-n-butoxyethyl]tin bis[alkylthiopropionate], where alkyl is, for example, 2-ethyl-n-hexyl, dodecyl, tridecyl or tetradecyl, and also organotin carboxylate, especially maleates or hemiester maleates, or mixtures of the organotin stabilisers mentioned above, or organic antimony compounds, such as antimony tris[isooctylthioglycolate] (isooctyl = 2-ethyl-n-hexyl).

The compositions of the invention can also contain customary antioxidants, for example:

1.1. Alkylated monophenols, e.g.

2,6-di-tert-butyl-4-methylphenol  
2-tert-butyl-4,6-dimethylphenol  
2,6-di-tert-butyl-4-ethylphenol  
2,6-di-tert-butyl-4-n-butylphenol  
2,6-di-tert-butyl-4-isobutylphenol  
2,6-dicyclopentyl-4-methylphenol  
2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol  
2,6-dioctadecyl-4-methylphenol  
2,4,6-tricyclohexylphenol  
2,6-di-tert-butyl-4-methoxymethylphenol

1.2. Alkylated hydroquinones, e.g.

2,6-di-tert-butyl-4-methoxyphenol  
2,5-di-tert-butylhydroquinone  
2,5-di-tert-amylhydroquinone  
2,6-diphenyl-4-octadecyloxyphenol

1.3. Hydroxylated thiodiphenyl ethers, e.g.

2,2'-thiobis(6-tert-butyl-4-methylphenol)  
2,2'-thiobis(4-octylphenol)  
4,4'-thiobis(6-tert-butyl-3-methylphenol)  
4,4'-thiobis(6-tert-butyl-2-methylphenol)

1.4. Alkylidenebisphenols, e.g.

2,2'-methylenebis(6-tert-butyl-4-methylphenol)  
2,2'-methylenebis(6-tert-butyl-4-ethylphenol)  
2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol]  
2,2'-methylenebis(4-methyl-6-cyclohexylphenol)  
2,2'-methylenebis(6-nonyl-4-methylphenol)  
2,2'-methylenebis(4,6-di-tert-butylphenol)  
2,2'-ethylidenebis(4,6-di-tert-butylphenol)  
2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol)  
2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol]  
2,2'-methylenebis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol]  
4,4'-methylenebis(2,6-di-tert-butylphenol)  
4,4'-methylenebis(6-tert-butyl-2-methylphenol)  
1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane  
2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol  
1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane  
1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane  
ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate]  
bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene  
bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate

1.5. Benzyl compounds, e.g.

1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene  
bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide  
isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate  
bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiolterephthalate  
1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate  
1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate  
dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate  
calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate

1.6. Acylaminophenols, e.g.

anilide of 4-hydroxylauric acid

anilide of 4-hydroxystearic acid

2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-s-triazine

octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate

1.7. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

with mono- or polyhydric alcohols, e.g. with

|          |                   |
|----------|-------------------|
| methanol | diethylene glycol |
|----------|-------------------|

|             |                    |
|-------------|--------------------|
| octadecanol | triethylene glycol |
|-------------|--------------------|

|                |                 |
|----------------|-----------------|
| 1,6-hexanediol | pentaerythritol |
|----------------|-----------------|

|                  |                                 |
|------------------|---------------------------------|
| neopentyl glycol | tris(hydroxyethyl) isocyanurate |
|------------------|---------------------------------|

|                       |                                  |
|-----------------------|----------------------------------|
| thiodiethylene glycol | bis(hydroxyethyl)oxyl<br>diamide |
|-----------------------|----------------------------------|

1.8. Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid

with mono- or polyhydric alcohols, e.g. with

|          |                   |
|----------|-------------------|
| methanol | diethylene glycol |
|----------|-------------------|

|             |                    |
|-------------|--------------------|
| octadecanol | triethylene glycol |
|-------------|--------------------|

|                |                 |
|----------------|-----------------|
| 1,6-hexanediol | pentaerythritol |
|----------------|-----------------|

|                  |                                 |
|------------------|---------------------------------|
| neopentyl glycol | tris(hydroxyethyl) isocyanurate |
|------------------|---------------------------------|

|                       |                                  |
|-----------------------|----------------------------------|
| thiodiethylene glycol | bis(hydroxyethyl)oxyl<br>diamide |
|-----------------------|----------------------------------|

1.9. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid,

e.g.

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylene-diamine

N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

Depending on the intended utility, the compositions of the invention may contain further conventional modifiers, for example lubricants (e.g. montan waxes or glycerol esters), fatty acid esters, paraffins, fillers, carbon black, asbestos, kaolin, talcum, glass fibres, fluorescent whitening agents, pigments, light stabilisers, UV absorbers,

flame retardants and/or antistats. Preferred modifiers are lubricants, pigments, processing assistants, fillers, antioxidants and/or light stabilisers.

The compositions of the invention preferably do not contain free aromatic carboxylic acids, especially those disclosed as component (d) in Japanese Patent Kokai Sho-54 11948.

The compositions of this invention can be processed to mouldings by conventional moulding methods, for example by extrusion, injection moulding, calendering or slush moulding (powder or plastisol). They can also be used as plastisols. PVC sheets for food packagings are preferably made therefrom.

The invention is illustrated in more detail by the following Examples, in which and throughout the description and claims, parts and percentages are by weight, unless otherwise stated.

Examples 1 - 4: The following PVC compositions are prepared by mixing the individual components (the amounts are expressed in parts by weight):

Table 1:

| Composition                             | Example |       |       |       |            |
|---|---------|-------|-------|-------|------------|
|   | 1       | 2     | 3     | 4     | Comparison |
| S-PVC (K-value 70) (®Corvic S71/102)    | 100     | 100   | 100   | 100   | 100        |
| dioctyl phthalate                       | 20      | 20    | 50    | 50    | 20         |
| thiodiethylene glycol bis(acetoacetate) | 1       | 2     | 1     | 2     | -          |
| epoxidised soybean oil (ESO)            | 5       | 5     | 5     | 5     | -          |
| zinc oleate                             | 0.15    | 0.15  | 0.15  | 0.15  | 0.15       |
| barium p-t-butylbenzoate                | 0.375   | 0.375 | 0.375 | 0.375 | 0.375      |
| diisodecylphenyl phosphite              | 0.525   | 0.525 | 0.525 | 0.525 | 0.525      |
| 2,6-di-t-butyl-4-methylphenol           | 0.075   | 0.075 | 0.075 | 0.075 | 0.075      |
| ®Shellsol A (=aromatic solvent mixture) | 0.375   | 0.375 | 0.375 | 0.375 | 0.375      |

### Static heat test

The compositions listed in Table 1 are rolled for 5 minutes at 180°C on a roll mill. Samples of the 0.3 mm rolled sheets obtained are subjected to heat ageing in a test oven (Mathis Thermotakter®, type LTF-ST) at 180°C. After the intervals of time indicated in Table 2, the Yellowness Index (YI) of each sample is determined in accordance with ASTM D 1925-70 (high YI values denote strong discolouration and therefore poor stability).

Table 2:

| Example    | YI after heat ageing (in minutes) |      |      |      |      |      |      |      |      |
|------------|-----------------------------------|------|------|------|------|------|------|------|------|
|            | 0                                 | 5    | 10   | 15   | 20   | 25   | 30   | 35   | 40   |
| 1          | 1.9                               | 2.0  | 2.1  | 2.4  | 3.2  | 4.4  | 6.4  | 8.7  | 12.1 |
| 2          | 2.2                               | 2.2  | 2.9  | 3.0  | 3.1  | 4.1  | 4.7  | 6.0  | 8.1  |
| 3          | 1.2                               | 1.2  | 1.3  | 1.6  | 2.3  | 3.8  | 5.0  | 7.5  | 9.5  |
| 4          | 0.9                               | 1.2  | 1.4  | 1.5  | 2.1  | 2.8  | 3.9  | 6.1  | 8.2  |
| comparison | 15.8                              | 16.5 | 19.4 | 22.3 | 28.7 | 33.3 | 37.0 | 42.4 | 43.6 |

### Pressed sheet

The compositions listed in Table 1 are rolled for 5 minutes at 180°C on a roll mill. The rolled sheets so obtained are pressed to 3 mm sheets for 3 minutes at 180°C/150 bar. The Yellowness Index (YI) of these sheets are determined as described above. The values are reported in Table 3.

Table 3:

| Example    | YI<br>("initial colour") |
|------------|--------------------------|
| 1          | 19.3                     |
| 2          | 16.2                     |
| 3          | 13.9                     |
| 4          | 13.7                     |
| comparison | 67.5                     |

Examples 5 - 8: The following PVC compositions are prepared by mixing the individual components (the amounts are expressed in parts by weight):

Table 4:

| Composition                              | Example |       |       |       | comparison |
|--|---------|-------|-------|-------|------------|
|  | 5       | 6     | 7     | 8     |            |
| S-PVC (K-value 70) (®Corvic S71/102)     | 100     | 100   | 100   | 100   | 100        |
| dioctyl phthalate                        | 20      | 20    | 50    | 50    | 20         |
| zinc oleate                              | 0.15    | 0.15  | 0.15  | 0.15  | 0.15       |
| Ca p-t-butylbenzoate                     | 0.375   | 0.375 | 0.375 | 0.375 | 0.375      |
| thiodiethylene glycol bis(acetoacetate)  | 1       | 2     | 1     | 2     | -          |
| epoxidised soybean oil (ESO)             | 5       | 5     | 5     | 5     | -          |
| diisodecylphenyl phosphite               | 0.525   | 0.525 | 0.525 | 0.525 | 0.525      |
| 2,6-di-tert-butyl-4-methylphenol         | 0.075   | 0.075 | 0.075 | 0.075 | 0.075      |
| ®Shellsol A (= aromatic solvent mixture) | 0.375   | 0.375 | 0.375 | 0.375 | 0.375      |

Preferably the compositions according to Examples 1 - 8 and the comparison compositions are prepared by mixing the metal carboxylates with ESO, diisodecyl phenylphosphite and Shellsol A to a stabiliser mixture. This mixture, together with the thiodiethylene glycol bis(acetoacetate) and the plasticiser (dioctyl phthalate), is then incorporated into the PVC.

The compositions listed in Table 4 are processed to rolled sheets as described for Examples 1 - 4. These sheets are subjected to heat ageing and the Yellowness Index is determined at 5 minute intervals. The results are reported in Table 5.

Table 5

| Example    | YI after heat ageing (in minutes) |     |     |     |      |      |      |      |       |
|------------|-----------------------------------|-----|-----|-----|------|------|------|------|-------|
|            | 0                                 | 5   | 10  | 15  | 20   | 25   | 30   | 35   | 40    |
| 5          | 3.1                               | 1.5 | 1.7 | 2.3 | 2.5  | 3.0  | 4.2  | 6.5  | 14.5  |
| 6          | 1.1                               | 1.6 | 1.9 | 1.8 | 2.3  | 3.1  | 4.2  | 6.6  | 10.8  |
| 7          | 0.9                               | 1.1 | 1.1 | 1.3 | 1.7  | 2.3  | 3.0  | 5.8  | 11.4  |
| 8          | 1.1                               | 1.1 | 1.1 | 1.4 | 1.6  | 2.0  | 3.2  | 6.2  | 13.3  |
| comparison | 3.6                               | 4.3 | 5.6 | 9.6 | 14.4 | 17.3 | 22.5 | 47.5 | 121.8 |

The compositions of Table 4 are further processed to pressed sheets as described for Examples 1 - 4 and the YI of these sheets is determined. The values are indicated in Table 6.

Table 6

| Example    | YI<br>("initial colour") |
|------------|--------------------------|
| 5          | 14.6                     |
| 6          | 14.5                     |
| 7          | 10.9                     |
| 8          | 10.6                     |
| comparison | 24.2                     |

Examples 9 and 10: The following PVC compositions are prepared by mixing the individual components (the amounts are expressed in parts by weight):

Table 7:

| Composition                             | Example |     | Comparison |
|---|---------|-----|------------|
|   | 9       | 10  |            |
| S-PVC (K-value 70) (@Corvic S71/102)    | 100     | 100 | 100        |
| dioctyl phthalate                       | 20      | 50  | 20         |
| zinc stearate                           | 0.1     | 0.1 | 0.1        |
| thiodiethylene glycol bis(acetoacetate) | 1       | 1   | -          |
| epoxidised soybean oil (ESO)            | 5       | 5   | -          |

The compositions of Table 7 are processed to sheets as described for Examples 1 to 4. The sheets are subjected to heat ageing and the Yellowness Index (YI) is determined at 5 minute intervals. The results are reported in Table 8.

Table 8:

| Example    | YI after heat ageing (in minutes) |     |     |      |      |     |      |
|------------|-----------------------------------|-----|-----|------|------|-----|------|
|            | 5                                 | 10  | 15  | 20   | 25   | 30  | 35   |
| 9          | 1.2                               | 1.5 | 1.7 | 2.9  | 4.3  | 6.8 | 9.3  |
| 10         | 1.4                               | 1.5 | 2.0 | 3.0  | 5.4  | 9.9 | 12.2 |
| comparison | 4.4                               | 5.0 | 8.2 | 25.1 | 31.9 | -   | -    |

The compositions of Table 7 are further processed to pressed sheets as described for Examples 1 - 4 and the Yellowness Index of these sheets is determined. The results are reported in Table 9.

Table 9:

| Example    | YI<br>("initial colour") |
|------------|--------------------------|
| 9          | 13.0                     |
| 10         | 10.8                     |
| comparison | 29.8                     |

Examples 11 - 13: The following PVC compositions are prepared by mixing the individual components (the amounts are expressed in parts by weight):

Table 10:

| Composition  | Example |     |            |
|--|---------|-----|------------|
|  | 11      | 12  | comparison |
| S-PVC (®Vinoflex S6514)                              | 100     | 100 | 100        |
| dioctyl phthalate                                    | 18      | 18  | 18         |
| zinc oleate  | 0.2     | 0.2 | 0.2        |
| Ba p-tert-butylbenzoate                              | 0.5     | 0.5 | 0.5        |
| thiodiethylene glycol bis(acetoacetate)              | 0.7     | 0.7 | -          |
| epoxidised soybean oil (ESO)                         | 3       | 3   | 3          |
| diisodecyl phosphite                                 | 0.7     | 0.7 | 0.7        |
| 2,6-di-tert-butyl-4-methylphenol                     | 0.1     | 0.1 | 0.1        |
| ®Shellsol A (= aromatic solvent mixture)             | 0.5     | 0.5 | 0.5        |
| 2-methyl-3-cyclohexyloxycarbonyl-4-phenyl-1H-pyrrole | -       | 0.2 | -          |

The compositions of Table 10 are rolled on a roll mill for 10 minutes at 180°C. Samples of the 0.3 mm rolled sheets so obtained are subjected to heat ageing in a test oven (Mathis Thermotakter® LTF-ST) at 190°C. The Yellowness Index (YI) of the samples is determined as described for Examples 1 - 4. The results are reported in Table 11.

Table 11:

| Example    | YI after heat ageing (in minutes) |      |      |      |      |
|------------|-----------------------------------|------|------|------|------|
|            | 10                                | 20   | 30   | 40   | 50   |
| 11         | 1.0                               | 2.3  | 2.6  | 3.1  | 5.4  |
| 12         | 0.9                               | 2.1  | 2.4  | 2.3  | 5.8  |
| comparison | 11.4                              | 15.0 | 15.1 | 12.7 | 10.9 |

The compositions of Table 10 are further processed to pressed sheets as described for Examples 1 - 4 and the Yellowness Index of these sheets is determined. The results are reported in Table 12.

Table 12

| Example    | YI<br>("initial colour") |
|------------|--------------------------|
| 11         | 24.7                     |
| 12         | 24.5                     |
| comparison | 64.7                     |

Example 13: The following PVC composition is prepared by mixing the individual components:

100 parts by weight of S-PVC (K value 64)  
15 parts by weight of dioctyl phthalate  
0.04 part by weight of zinc neodecanoate  
0.7 part by weight of thiodiethylene glycol bis(acetoacetate)  
5 parts by weight of epoxidised soybean oil (ESO)  
0.3 part by weight of 2-methyl-3-cyclohexyloxycarbonyl-4-phenyl-1H-pyrrole.

This composition is processed to a sheet as described for Examples 1 - 4 and the sheet is subjected to heat ageing as described therein. The Yellowness Index is determined at 5 minute intervals. The following YI values are obtained:

|             |     |     |     |     |     |     |      |
|-------------|-----|-----|-----|-----|-----|-----|------|
| time (min.) | 5   | 10  | 15  | 20  | 25  | 30  | 35   |
| YI          | 0.4 | 1.6 | 2.5 | 4.0 | 6.4 | 9.8 | 13.4 |

What is claimed is:

1. A stabilised polymer composition comprising

- a) 100 parts of a chlorinated thermoplastic,
- b) 0.7 to 2 parts of thiodiethylene glycol bis(acetoacetate) of formula  $(H_3CCOCH_2COOCH_2CH_2)_2S$ ,
- c) 0 to 0.5 part of at least one calcium, barium and/or magnesium salt of an aliphatic  $C_8-C_{24}$  monocarboxylic or  $C_8-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- d) 0.01 to 0.2 part of at least one zinc salt of an aliphatic  $C_8-C_{24}$  monocarboxylic or  $C_8-C_{24}$  hydroxymonocarboxylic acid or of benzoic acid or tert-butylbenzoic acid,
- e) 3 to 10 parts of epoxidised unsaturated fatty acid esters, and
- f) 10 to 70 parts of at least one organic plasticiser.

2. A composition according to claim 1, wherein component c) is a calcium or magnesium salt or a mixture thereof.

3. A composition according to either claim 1 or claim 2, wherein the chlorinated thermoplastic is a vinyl chloride homopolymer, a copolymer of vinyl chloride with unsaturated comonomers, a mixture of said polymers with one another or a mixture of said polymers with other mono- or copolymers.

4. A composition according to either claim 1 or claim 2, which contains 0.8 to 1.5 parts of component b).

5. A composition according to either claim 1 or claim 2, which contains 0.01 to 0.5, preferably 0.05 to 0.4, part of component c).

6. A composition according to any one of claims 1, 2 or 5, wherein component c) is a calcium salt.

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